



Isoconversional kinetic analysis of olive pomace decomposition under torrefaction operating conditions

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ABSTRACT

Kinetic analysis of the olive pomace thermal degradation in the temperature range of interest for torrefaction was performed by using non-isothermal thermogravimetric measurements at different heating rates, ranging from 2 to 40 °C/min. A comparison is presented between two selected integral isoconversional methods, i.e., the nonlinear Vyazovkin incremental approach, which is more accurate but time-consuming, and the linear Ozawa–Flynn–Wall (OFW) method, which is less accurate but computationally simpler. Results show that the values of the activation energy by the OFW method are consistent with the ones provided by the Vyazovkin approach. This implies that the OFW method, more user-friendly compared to the Vyazovkin procedure, is suitable for studying the torrefaction kinetics of residual biomass, such as olive pomace. The reliability of the OFW method was further confirmed by the successful application of the derived kinetic data to reproduce (i.e., predict) experimental TG curves not included in the kinetic computations.

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1. Introduction

In the view of shortage of fossil fuels and with the increasing concerns regarding human impacts on the environmental, renewable energy sources and waste materials play an important role as a viable alternative to fossil fuels for both energy generation and production of chemicals [1]. Now on the brink of commercialization, torrefaction – a relatively new thermochemical treatment of biomass carried out at quite low temperatures (200–300 °C), atmospheric pressure and in an inert environment – is currently considered as a key process in facilitating raw biomass (i.e., grass, woody, crop or processing industry residues) market growing for energy applications, due to its potential to convert any organic material into a high-energy-density solid fuel with superior properties in view of transport, handling, storage and in many major thermochemical end-use applications (e.g., co-firing in coal-fired power stations and gasification-based production of gaseous biofuels or bio-chemicals) [2].

Olive pomace is the solid and wet by-product generated by olive-oil extraction industries. Among other possibilities of utilization (e.g. animal feed, production of fertilizer, composting, etc.), the thermal treatment is appealing because it is an intensive and effective method for converting the olive pomace into energy [3], avoiding release of pollutants and odors as well as uncontrolled fermentation [4]. Several studies [3,4] have been conducted on energy generation from the olive pomace;

however, no one includes torrefaction as pretreatment, which is able to produce an intermediate and stable material and does not suffer high moisture content, low energy density, hygroscopic behavior and limited storage life.

With this background, the primary aim of the present study was to propose a set of kinetic parameters to be used as an input to future computer-based simulations of the olive pomace torrefaction, which can be used to guide laboratory experiments as well as to generate and evaluate alternative designs [5–7] for renewable energy projects.

Non-isothermal thermogravimetric analysis (TGA) was selected as the experimental technique to obtain kinetic data due to its ability to overcome one of the major problems associated with standard isothermal experiments, i.e. the warm-up time. Actually, during the initial non-isothermal time of an isothermal TGA test the sample typically undergoes some transformations that are likely to affect the results of the subsequent kinetic analysis [8]. In addition, when a too slow heating rate is applied, the weight loss taking places during the warm-up phase is not negligible, which complicates the interpretation and deduction of kinetic data [9].

Even though traditional model fitting approaches, including single or multi-step reaction mechanisms and/or single or multiple pseudo-component models [9–13], have found to date the almost exclusive application in biomass thermochemical conversion kinetic analysis [14], a “model-free” approach based on integral isoconversional methods was adopted in this paper. This choice was motivated by the fact that the model fitting procedures, when applied to non-isothermal data, produce Arrhenius parameters strongly depending on the adopted reaction

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model. As a consequence, they are so uncertain and variable that they cannot be meaningfully used for predicting the behavior of a substance over the range of experimental temperatures [8]. Conversely, model-free techniques do not require any assumption of reaction models, thus avoiding possible errors associated with such a choice. In addition, yielding kinetic parameters as a function of either conversion (isoconversional analysis) or temperature (non-parametric kinetics) [15], these methods make it possible to study the overall kinetics throughout the whole range of experimental conversions and temperatures also for complex solid state processes, like biomass thermal decomposition, which usually involve several steps with different activation energies.

Among the large number of differential and integral isoconversional methods to date developed, two integral multiple temperature-programmed methods, i.e., the linear Ozawa–Flynn–Wall (OFW) and the nonlinear Vyazovkin incremental methods, were selected to be comparatively applied in this work for the kinetic analysis of olive pomace torrefaction from non-isothermal TGA data. It is well-known [8, 16–18] that, in a comparison between the two methods, the OFW procedure is computationally simpler, but less accurate.

In addition to proposing a set of kinetic parameters for a future conceptual process design of olive pomace torrefaction, this work aims to provide a further insight into the application of the model-free isoconversional methods, most commonly used for the kinetic analysis of thermally simulated process involving polymers [19] or other complex organic compounds [20], also in the field of biomass thermochemical conversion processes.

2. Materials and methods

2.1. Feedstock sampling and characterization

The olive pomace used in this research work was suitably sampled from the accumulated residues of a three-phase olive mill located in Frasso Telesino (41° 9' 22" N, 14° 31' 48" E) in Campania region, in November 2013. In order to preserve their original qualities and to prevent the microbial degradation before further analyses, all samples, just collected, were sealed in a plastic bag and stored at –20 °C. Prior to use, representative fractions of this agro-industrial waste were milled using a knife mill to a particle size lower than 1 mm, afterwards, if required, oven-dried at 105 °C for about 12 h and then stored in a desiccator.

Proximate (TG 701 LECO Thermogravimetric analyzer), ultimate (CHN 2000 and SC 144 DR LECO analyzer) and calorific (Parr 6200 Calorimeter) analyses were performed in order to obtain the basic properties as a fuel of this agro-industrial residue. The results are presented in Table 1.

The indicative chemical composition of the olive pomace from a three-phase centrifugation process is also shown in Table 1, based on data reported in the literature [21].

2.2. Experimental methods

Thermogravimetric analyses were carried out in a TA Instruments analyzer Q600 SDT. Nitrogen was used as the purge gas at a flow rate of 100 ml/min to ensure an inert atmosphere and to prevent secondary reactions by volatiles produced during the solid thermal decomposition. During each run, approximately 10–15 mg of oven-dried samples, with a size of 0.5–1 mm, were placed in an aluminum oxide crucible inside the furnace chamber of the microbalance. Dynamic runs at five different heating rate programs, i.e., 2, 5, 10, 20, 40 °C/min, were carried out over the temperature range from room temperature to about 1000 °C to be used for the kinetic computations.

In addition to this series of constant heating rate runs, two isothermal experiments at 250 °C and 300 °C were also performed to check the reliability of the employed kinetic approach. During the isothermal run, the dried sample was first heated up to a temperature of 105 °C,

Table 1

Proximate, ultimate, calorific and chemical analyses of olive pomace.

	Olive pomace
Moisture (wt.%, as received)	62.71
<i>Proximate analysis (wt.%, dry basis)</i>	
Volatile matter	82.06
Fixed carbon	15.76
Ash	2.18
<i>Ultimate analysis (wt.%, dry basis)</i>	
C	52.58
N	0.78
H	7.23
S	<0.01
Ash	2.18
O (by diff.)	37.23
HHV (MJ/kg, dry basis)	21.88
LHV (MJ/kg, dry basis)	20.49
<i>Chemical composition (wt.% dry basis) [21]</i>	
Hemicelluloses	15.91
Celluloses	34.90
Lignin	20.51
Fats and oils	7.82
Proteins	6.89

which was held for 10 min. Then the temperature was increased to the desired test value at a heating rate of 5 °C/min and kept constant for 7 h. Note that the aforesaid isothermal time excludes the warm-up phase, which globally lasted for about 1 h. Both thermogravimetric and differential temperature measurements were recorded simultaneously during each test.

2.3. Non-isothermal kinetic analysis

All the integral curves derived from dynamic heating rate experiments (TGA) were used in the kinetic analysis, after being converted to the plot of conversion (α) versus temperatures by Eq. (1)

$$\alpha = \frac{m(T_i) - m(T)}{m(T_i) - m(T_f)} \quad (1)$$

where $m(T)$, $m(T_i)$ and $m(T_f)$ designate the instantaneous sample weight, the initial sample weight and the final sample weight, respectively. To provide the kinetic analysis with a standard reference, the initial and the final sample weights were identified, for each run, at 150 °C and 450 °C, which correspond to the temperature range where olive pomace decomposition mainly occurs (see detailed discussion in Section 3.1). The motivation for this choice lies in the fact that, although the major objective of torrefaction is substantially the complete degradation of its hemicellulose content, it is unavoidable that such decomposition takes place without a simultaneous and partial degradation of the other biomass components, in particular the cellulose fraction [22].

As mentioned in Introduction, the model-free kinetic approach based on two integral isoconversional methods, i.e., the Ozawa–Flynn–Wall (OFW) and the Vyazovkin ones, was employed in this study in order to evaluate the effective activation energy (E_a) as a function of the conversion degree (α).

Although it is traditionally expected that a kinetic analysis produces a description of a process in terms of the so-called kinetic triplet [8], i.e., the reaction model and Arrhenius parameters ($f(\alpha)$, E and A), no further computations aimed at evaluating the pre-exponential factor and the reaction model were performed in this study. The reason is that the sole goal of the kinetic analysis carried out in this study was to predict the characteristic time needed to achieve a prefixed conversion degree under conditions typical of torrefaction that could be a valuable result for designing a torrefaction reactor. As shown by

Vyazovkin et al. [17], the knowledge of the E_α vs α dependence is by itself sufficient to do this.

Following the pragmatic guidance from the ICTAC Kinetics Committee [17], the reliability of the global activation energy obtained from the dynamic TGA runs, was checked by simulating isothermal profiles, obtained from tests not used in the kinetic analysis. To provide a standard reference for all the experimental variables dependent on the conversion degree by both the isothermal and non-isothermal TG, during this validation step, the aforesaid independent variable, which, by definition, is a normalized form of the experimental weight loss, was re-defined as follows:

$$\alpha^* = \frac{m(t_i) - m(t)}{m(t_i)} \quad (2)$$

where $m(t)$ and $m(t_i)$ designate the instantaneous sample mass and the initial sample mass (i.e., sample mass at 150 °C), respectively.

Simulation of the experimental curves was obtained by means of the following expression [12]:

$$t_{\alpha^*} = \frac{1}{\beta} \int_0^{T_{\alpha^*}} \exp\left(-\frac{E_{\alpha^*}}{RT}\right) dT \quad (3)$$

$$\exp\left(-\frac{E_{\alpha^*}}{RT_0}\right)$$

where t_{α^*} is the time to reach the conversion degree α^* at an arbitrary temperature T_0 (i.e., 250 °C and 300 °C) under isothermal conditions, $\beta = dT/dt$ is the constant heating rate, T is the absolute temperature, T_{α^*} is the temperature at which the conversion α^* is experimentally achieved at the heating rate β , R is the gas constant and E_{α^*} is the activation energy related to the extent of conversion, α^* .

The integral in Eq. (3) was solved based on the values of E_{α^*} obtained by the application of the OFW method and experimental T_{α^*} by dynamic thermal curves recorded at the same heating rate of the simulated isothermal ones (i.e., 5 °C/min). Specifically, in the present study, Eq. (3) was used to compute the time at which different conversion degrees were reached at 250 °C and 300 °C, under isothermal conditions.

2.4. Ozawa–Flynn–Wall and Vyazovkin isoconversional methods for the determination of the apparent E_α dependence on α

Model-free isoconversional methods rest upon the isoconversional principle, which states that, at a constant extent of conversion, the reaction rate is a function only of the temperature [19].

Different integral isoconversional methods originate from the various ways of integrating the following single step kinetics Eq. (4):

$$\frac{d\alpha}{dt} = A \cdot \exp\left(-\frac{E}{RT}\right) \cdot f(\alpha) \quad (4)$$

where t is the time, A is the pre-exponential factor, E is the activation energy, T is the absolute temperature, R is the gas constant, α is the conversion degree of the process that can be determined from TGA runs as a fractional mass loss and $f(\alpha)$ is the reaction model, that is a function depending solely on α .

For a constant heating rate program, where the temperature is raised at a constant rate $\beta = dT/dt$, the integration of Eq. (4), in particular, yields:

$$g(\alpha) \stackrel{\text{def}}{=} \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T \exp\left(-\frac{E}{RT}\right) dT = \frac{A}{\beta} I(E, T) \quad (5)$$

where $g(\alpha)$ is the integrated form of the reaction model $f(\alpha)$ and $I(E, T)$ is the temperature integral. Since the temperature integral in Eq. (5) has no analytical solution, it is typically solved by using approximations or numerical integration, each of which is at the base of a different integral isoconversional method.

It is worth noting that, although the use of approximation of the temperature integral instead of an accurate numerical method induces an error in the value of the activation energy, such approximations are typically preferred since they lead to the simplest final plots (i.e., linear) yielding the activation energy very quickly [16].

The application of the very crude Doyle's approximation [25] leads to the following linear Eq. (6) that is at the base of the popular linear Ozawa–Flynn–Wall method used in this work:

$$\ln \beta_i = \ln \left(\frac{A \cdot E_\alpha}{g(\alpha) \cdot R} \right) - 5.3305 - 1.052 \frac{E_\alpha}{RT_{\alpha,i}} \quad (6)$$

where $T_{\alpha,i}$ is the temperature at which the conversion α is experimentally achieved at the heating rate β_i and the subscript i is a number representing experiments performed at different heating rates, β_i . Through the Eq. (6), this method allows to obtain the value of the apparent activation energy E_α at a fixed conversion value α , from the slope of the straight line generated in the plot of $\log(\beta_i)$ versus $1/T_{\alpha,i}$, for a number n of TGA experiments carried out at different heating rates (β_i).

In this study, by determining the value of E_α for each conversion degree in the range of $\alpha = 0.05$ – 0.95 with a step of 0.05 , the dependence of E_α on α was obtained.

According to the more accurate nonlinear Vyazovkin method, for each given value of α , the apparent activation energy value, E_α , can be determined by minimizing the following function $\Phi(E_\alpha)$,

$$\Phi(E_\alpha) = \sum_{i=1}^n \sum_{j \neq i}^n \frac{I(E_\alpha, T_{\alpha,i}) \cdot \beta_j}{I(E_\alpha, T_{\alpha,j}) \cdot \beta_i} \quad (7)$$

where the temperature integrals are solved numerically, with a very time-consuming procedure.

In this work, the standard Solver function, contained in the Microsoft Excel spreadsheet package, was used to obtain the value of E_α minimizing the function $\Phi(E_\alpha)$. This solver applies the Generalized Reduced Gradient (GRG) nonlinear solving algorithm that is one of the most robust nonlinear programming methods [26]. For each run, in particular, after substituting experimental values of T_α and β into the nonlinear Eq. (7), the value of each temperature integral was found by applying the trapezoidal integration rule with a temperature step of 10^{-2} K and assuming the constancy of E_α only for a small integral conversion $\Delta\alpha$ ($= 0.05$) according to the formula [19]:

$$I^*(E_\alpha, T_\alpha) = \int_{T_{\alpha-\Delta\alpha}}^{T_\alpha} \exp\left(-\frac{E_\alpha}{RT}\right) dT \quad (8)$$

Note that the original method [27] uses the regular integration from 0 to T_α , as a result of which each value of E_α becomes averaged over the region $0 - \alpha$, and the whole E_α dependence undergoes an undesirable flattening. However, the methods were subsequently modified to adequately account for a variation of E_α with α [28]. To do this the regular integration from 0 to T_α was replaced with the integration over small temperature segments as in Eq. (8).

3. Results and discussions

3.1. Thermogravimetric analysis

Mass loss (TG) and derivative mass loss (DTG) curves for the thermal decomposition of olive pomace at different heating rates (i.e., 2, 5, 10, 20, 40 °C/min) are shown in Fig. 1.

As expected, due to the presence of residual oil that inevitably and in a variable percentage, remains trapped within the matrix of this residue after the extraction process, the olive pomace does not show the typical thermogravimetric behavior of a standard lignocellulosic biomass (mainly composed of hemicellulose, cellulose and lignin), which is characterized

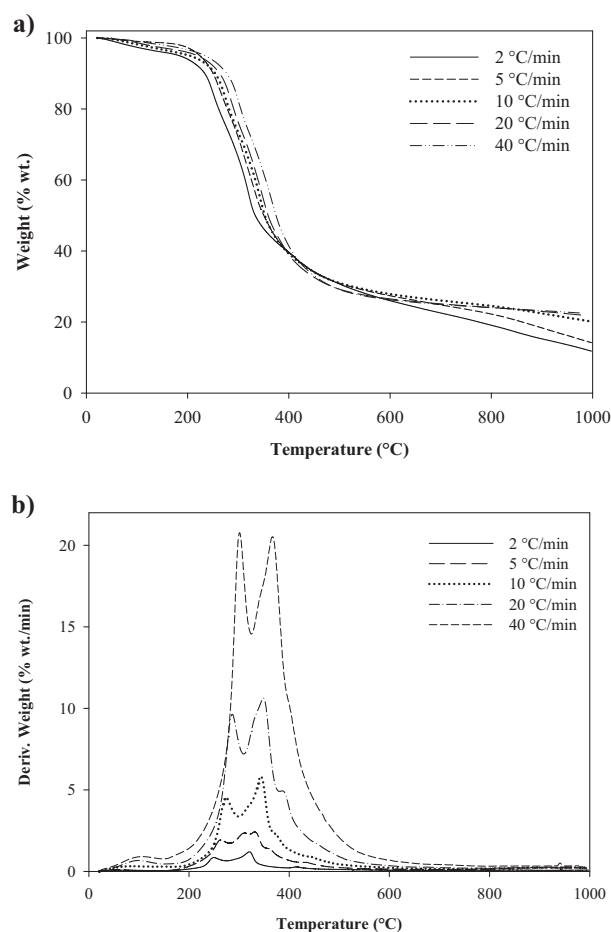


Fig. 1. Olive pomace (a) TG and (b) DTG curves at different heating rates (2, 5, 10, 20, 40 °C/min) recorded in nitrogen atmosphere with a purge rate of 100 ml/min from ambient temperature to 1000 °C.

by three decomposition phases, in addition to the first one due to the removal of water and water soluble components in the sample. In fact, as shown by the thermogram recorded with a heating rate of 2 °C/min (Fig. 1) and zoomed in greater detail for better readability in Fig. 2, five distinct weight loss phases could be identified on the TG curve, related to the four downward peaks observed on the DTG curve, being the last three partially overlapping, and to the final gently sloping baseline. The first phase, corresponding to the reduction in mass (≈ 4.5 wt.% of the total

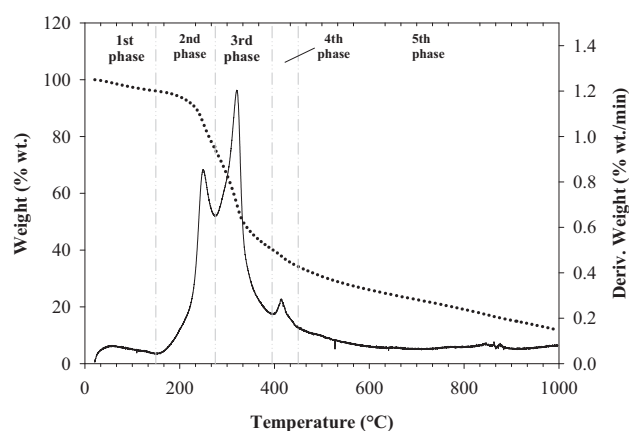


Fig. 2. Olive pomace TGA (---) and DTG (—) curves at $\beta = 2$ °C/min recorded in nitrogen atmosphere with a purge rate of 100 ml/min. Vertical dashed-dotted lines delimit the five distinct weight loss phases.

mass loss) at temperature lower than 150 °C, can be attributed to the removal of water and light volatiles. The second phase, between 150 and 275 °C, which accounts for approximately 23.4 wt.% of the total mass loss, can be attributed mainly to the thermal degradation of hemicellulose fraction, which is the most reactive part of a biomass and typically decomposes in the range of 220–280 °C [22], and partly to the beginning of cellulose decomposition. The third phase (275–395 °C) which accounts for approximately 40 wt.% of the total mass loss, in turn can be attributed mainly to the thermal degradation of cellulose, which typically degrades in a higher temperature range of 240–350 °C [22] and partly to the end of hemicellulose decomposition. In the fourth phase, over the temperature range from 395 to 450 °C, there was a negligible weight loss (≈ 6.9 wt.% of the total mass loss) that can be attributed to the thermal decomposition of the olive pomace oily fraction. Finally, the fifth phase located between 450 and 1000 °C corresponds to the slow (i.e., without a characteristic peak) weight loss of lignin whose degradation typically occurs over a wider temperature range [23] as a consequence of the different thermal stability of the various oxygen functional groups from its structure [24]. This stage contributes to a weight loss of 25.2 wt.% of the total mass loss.

The characteristics related to all decomposition phases such as the starting temperature, T_i , the ending temperature, T_f , the weight loss, the maximum weight loss rate, W_{max} , and the temperature where this rate occurred, T_{max} , were exactly determined for all the studied heating rates (i.e., 2, 10, 20, 40 °C/min) and their values are given in Table 2.

It is well-known that the heating rate affects the TG and DTG curves considerably [29]. More specifically, it can change the curve shape and characteristic temperatures indicated in a curve. Fig. 1 shows the heating rate effects on the TG (Fig. 1(a)) and DTG (Fig. 1(b)) curves of olive pomace. It appears that higher heating rates gave globally a lower weight loss (or conversion). In addition, when the heating rate increases, TGA curves are shifted toward the right and the peaks of DTG curves are slightly shifted toward higher temperatures. Accordingly, all the characteristic temperatures in Table 2 were shifted to higher values with increasing heating rate. The findings observed in this study mirror those of the previous investigations that have examined the same effects [30].

Fig. 3 shows the weight loss (TG) curves and derivative of the mass loss curves (DTG) obtained from two isothermal runs performed at 250 °C (a) and 300 °C (b), under inert atmosphere. It also includes the temperature versus time plots describing the temperature program used. At 250 °C over a test time of 475 min (Fig. 3(a)), the total weight loss of olive pomace sludge is 36.42 wt.%. The most evident and considerable weight loss (~ 49 wt.% of the total mass loss), however, occurs in a narrower time range (approximately 40–75 min) as highlighted by the spike in DTG, most likely as a result of the predominant decomposition of hemicellulose.

Note that, despite the warm-up phase that is relatively short in this test due to the relatively low temperature (250 °C) adopted, the weight loss during this stage is not negligible, as it accounts for approximately 30 wt.% of the total mass loss. This supports what has been said previously about the limitations of a kinetic analysis based on isothermal data, with regard to the error introduced by the sample decomposition during the warm-up phase. As indeed observed in the present work, the weight loss during the non-isothermal period of an isothermal experiment may be considerable, despite a relatively short warm-up phase occurs, since it also depends on the specific reactivity of the sample.

Moving from 250 °C to 300 °C and keeping the two runs of equal length, the total conversion of olive pomace increases by about 20.87% (Fig. 3(b)), about 50% of the total mass converted being lost during the warm-up phase. The onset of a second peak in the DTG curves displayed in Fig. 3(b), confirms that at more severe torrefaction conditions (300 °C), cellulose is more deeply degraded.

3.2. Global kinetic analysis

The OFW plots of $\ln(\beta_i)$ versus $1/T_{\alpha,i}$ for different values of conversion (α) are shown in Fig. 4. For each value of α , the apparent activation

Table 2
Olive pomace thermal decomposition at different heating rates.

Heating rate (K/min)	First decomposition phase					Second decomposition phase					Third decomposition phase					Fourth decomposition phase					Fifth decomposition phase						
	T _i (°C)	T _f (°C)	T _{max} (°C)	W _{max} (wt.%/min)	Weight loss (wt.%)	T _i (°C)	T _f (°C)	T _{max} (°C)	W _{max} (wt.%/min)	Weight loss (wt.%)	T _i (°C)	T _f (°C)	T _{max} (°C)	W _{max} (wt.%/min)	Weight loss (wt.%)	T _i (°C)	T _f (°C)	T _{max} (°C)	W _{max} (wt.%/min)	Weight loss (wt.%)	T _i (°C)	T _f (°C)	T _{max} (°C)	W _{max} (wt.%/min)	Weight loss (wt.%)		
2	21.5	152.2	51	0.1	3.6	152.2	274.9	249.5	0.8	20.9	249.5	395.7	320.5	1.2	35.32	395.7	445.4	413.5	0.3	6.0	445.4	1000	–	–	–	21.86	
10	21.1	175.4	80.9	0.3	3.7	175.4	298.5	272.7	4.5	24.0	298.5	436.7	343.1	5.8	36.8	436.7	467.2	442.5	0.9	2.3	467.2	1000	–	–	–	12.34	
20	48.9	282.2	96.1	0.7	3.5	182.2	309.5	286.6	9.6	23.7	309.5	378.5	347.8	10.6	28.73	378.5	415.8	388.9	4.9	7.56	415.8	1000	–	–	–	14.52	
40	25.2	185.9	97.9	0.9	2.8	185.9	324.5	300.2	20.8	24.77	324.5	470.2	366.7	20.6	41.25	–	–	–	–	–	–	470	1000	–	–	–	8.48

energy was calculated from the slope of the plotted regression line. The results obtained and the correlation coefficient (R^2) are listed in Table 3 together with the values of the apparent activation energy E_α obtained by using the nonlinear Vyazovkin procedure.

By comparing the aforesaid values of E_α (Table 3), it results that the error in the activation energy, as induced by the approximation of the temperature integral used to derive the simplest linear equation (i.e., Eq. (6)) on which the OFW method is based, may be considered reasonably small, being lower than the conventionally accepted 10% level in the activation energy [8]. Hence, with regard to the olive pomace decomposition, this means that the linear procedure may be conveniently used for the computation of reliable kinetic parameters. The greatly reduced computational load as compared to the more accurate nonlinear Vyazovkin incremental procedure just offsets a slightly higher error in the activation energy determination.

Fig. 5 shows the dependence of the activation energy on the extent of olive mill sludge conversion, as computed by both the linear and nonlinear methods, in a temperature range of interest for a torrefaction process. A small decrease in the E_α appears at low conversion degree (≤ 0.15), followed by an almost constant (no multiple peaks and/or shoulders) value of E_α over the conversion range $0.2 \leq \alpha \leq 0.70$ and by a subsequent rapid rise of E_α for α ranging between 0.75 and 0.95.

It is worth noting that such trend reflects, in a way, the three main steps of thermal decomposition of olive mill sludge (Fig. 1(b)), falling in the range of 150–450 °C where the kinetic evaluation particularly focused on. A comparison of the two trends, based on the values of the conversion degree, reveals that the first trend change observed in Fig. 5 at $\alpha = 0.15$ corresponds roughly to the maximum of the second peak of the DTG curves in Fig. 1(b) as well as the second trend change, at $\alpha = 0.7$, corresponds roughly to the maximum of the third peak of the DTG curves in Fig. 1(b). Consistently, the lower the value of activation energy in Fig. 5 the higher the weight loss rate in Fig. 1(b).

Anyway, the apparent activation energy as given by both the linear (i.e., ranging between 167.94 and 994.09 kJ·mol^{−1}) and nonlinear (i.e., ranging between 162.59 and 1069.74 kJ·mol^{−1}) procedures globally shows the same increasing dependence upon the conversion degree in the range of 0.05–0.95. This trend can be qualitatively explained by the fact that the residual biomass becomes increasingly more reluctant to further decomposition in a N₂ atmosphere as the conversion progresses.

Note, however, that the lower value of the correlation coefficient at $\alpha = 0.90$ –0.95 (Table 3) implies that the corresponding values of E_α might be less reliable.

As it is well-known, during the torrefaction process, a biomass typically loses 20–35 wt.% of its initial mass, mainly as a consequence of the complete degradation of hemicellulose and of the partial decomposition of cellulose. Accordingly, this means that over the range of interest for torrefaction (i.e., $\alpha \leq 0.55$ based on Eq. (2)) in Fig. 5, the apparent activation energy calculated for the thermal decomposing of olive mill sludge may be regarded as roughly constant, amounting to about 200 kJ·mol^{−1} by averaging E_α over α . This finding suggests that the torrefaction of olive pomace can be adequately described by a single-step model, which provides an adequate kinetic representation of a multi-step process having a single rate-limiting. Note that the averaging of E_α is a procedure that may be justified only when a change in E_α as a function of α is just a few percent units of the mean value, but not when such a change is comparable to the mean value [8].

On the basis of the apparent activation energy dependence on the extent of decomposition, as obtained by the OFW method, curves representing the conversion of olive pomace at two different isothermal conditions (i.e., 250 °C and 300 °C) were obtained by the use of Eq. (3). To give an indication of the reliability of the kinetic approach employed, the results of the above prediction were then compared with data obtained by the isothermal TG analysis (Fig. 3), not included in the kinetic computations.

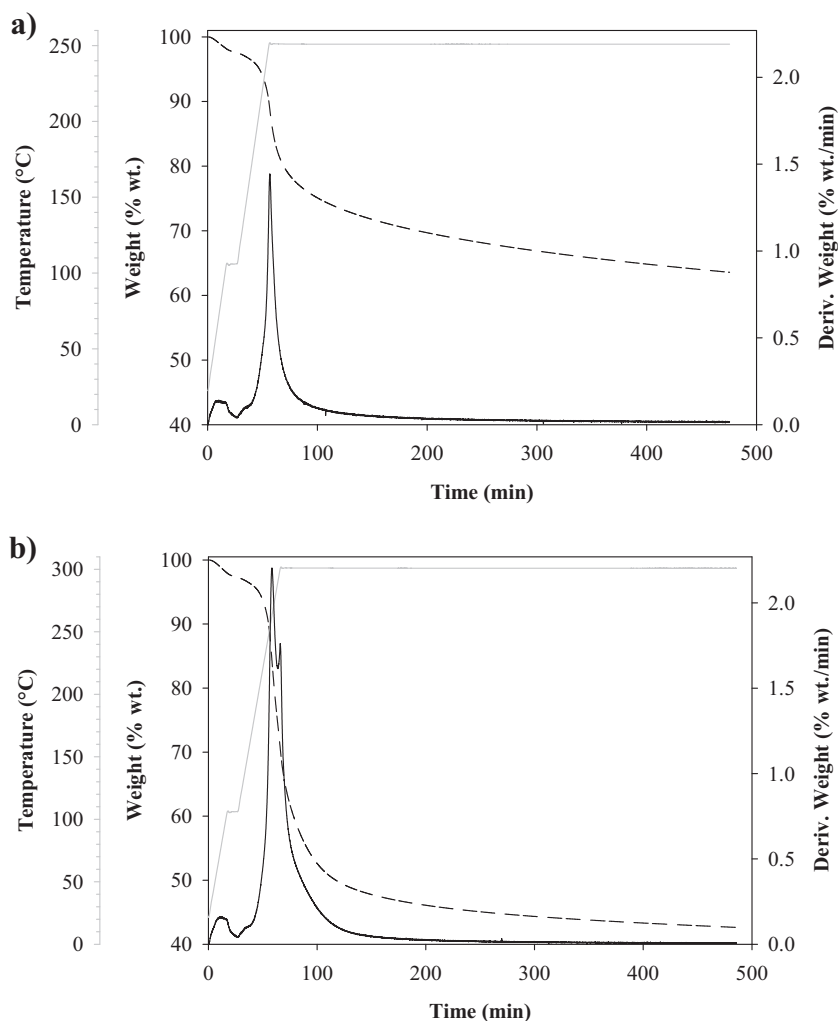


Fig. 3. TGA (—) and DTG (---) curves of olive pomace recorded under an inert atmosphere, following a quasi-isothermal, pre-set temperature program (—) up to: a) 250 °C and b) 300 °C.

It is worth observing that, according to the ICTAC Kinetics Committee [17], the validation of the computed kinetic parameters by demonstrating that they can be used to satisfactorily predict (reproduce) experimental curves not included in computation rather than experimental curves used to derive the same parameters is a more rigorous approach.

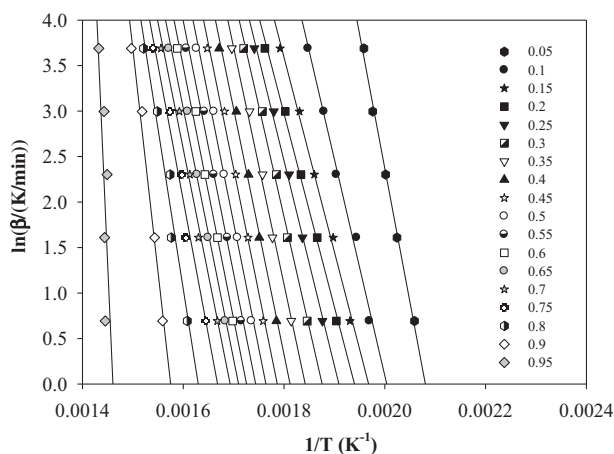


Fig. 4. Isoconversional Ozawa–Flynn–Wall plot for olive pomace decomposition at different values of conversion.

Table 3

Activation energy for olive pomace decomposition by the Vyazovkin and Ozawa–Flynn–Wall methods. R^2 corresponds to the linear fitting in Fig. 4.

α (—)	Vyazovkin method	Ozawa–Flynn–Wall method			
	E_{α} (kJ mol ⁻¹)	E_{α} (kJ mol ⁻¹)	Plot equation	R^2	Relative error ^a
0.05	244.76	232.85	$\ln\beta = -29,463 T^{-1} + 61$	1.00	0.05
0.10	189.59	187.78	$\ln\beta = -23,760 T^{-1} + 48$	0.99	0.01
0.15	162.59	169.16	$\ln\beta = -21,404 T^{-1} + 42$	0.99	0.04
0.20	169.68	167.94	$\ln\beta = -21,250 T^{-1} + 41$	1.00	0.01
0.25	196.57	177.87	$\ln\beta = -22,506 T^{-1} + 43$	1.00	0.09
0.30	215.39	192.07	$\ln\beta = -24,303 T^{-1} + 46$	0.99	0.1
0.35	226.59	205.87	$\ln\beta = -26,050 T^{-1} + 48$	0.98	0.09
0.40	227.20	212.32	$\ln\beta = -27,005 T^{-1} + 49$	0.99	0.07
0.45	225.56	216.11	$\ln\beta = -27,345 T^{-1} + 49$	0.99	0.04
0.50	228.35	218.46	$\ln\beta = -27,643 T^{-1} + 49$	0.99	0.04
0.55	227.73	219.27	$\ln\beta = -27,745 T^{-1} + 48$	0.99	0.04
0.60	227.08	219.80	$\ln\beta = -27,812 T^{-1} + 48$	0.99	0.03
0.65	222.22	218.37	$\ln\beta = -27,631 T^{-1} + 47$	0.99	0.02
0.70	228.57	219.40	$\ln\beta = -27,762 T^{-1} + 47$	0.99	0.04
0.75	263.22	219.40	$\ln\beta = -27,762 T^{-1} + 49$	0.97	0.2
0.80	319.52	277.71	$\ln\beta = -35,140 T^{-1} + 57$	0.96	0.1
0.85	407.85	387.98	$\ln\beta = -49,093 T^{-1} + 77$	0.99	0.04
0.90	602.22	521.33	$\ln\beta = -65,966 T^{-1} + 100$	0.92	0.1
0.95	1069.74	994.09	$\ln\beta = -125,786 T^{-1} + 183$	0.44	0.07

^a Relative error = $|E_{OFW} - E_{Vyazovkin}| / E_{Vyazovkin}$

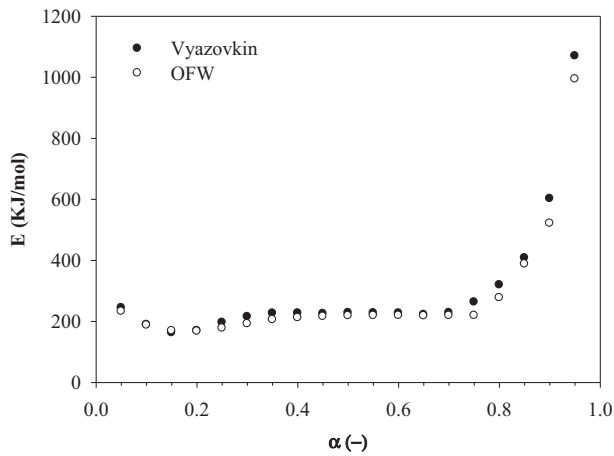


Fig. 5. Dependence of the activation energy on the conversion degree as determined by the isoconversional Vyazovkin and Ozawa–Flynn–Wall methods.

As shown in Fig. 6(a)–(b), predictions are in excellent agreement with results from isothermal measurements. It is recalled that the dotted lines in Fig. 6(a)–(b) were derived from the isothermal data shown in Fig. 3(a)–(b), respectively, whereas simulation results

(i.e., circle symbols) were calculated on the basis of the dynamic TG curves (Fig. 1(a)), via the OFW procedure.

Note that, since the above simulations were performed by using Eq. (3) that allows to compute the time at which a given conversion is reached at an arbitrary temperature under isothermal conditions, the comparison was focused only on the isothermal region of the thermograms at $T = 250\text{ }^{\circ}\text{C}$ (Fig. 3(a)) and at $T = 300\text{ }^{\circ}\text{C}$ (Fig. 3(b)) and, more specifically, limited to the narrow time range ($t \leq 150\text{ min}$) where the most rapid weight loss occurs.

4. Conclusion

Decomposition kinetics of olive pomace in the temperature range of interest for torrefaction were investigated by the non-isothermal TG at different heating rates (i.e., 2, 5, 10, 20, 40 K/min). The dependence of the apparent activation energy on the conversion degree was determined by means of a model-free approach based on two integral isoconversional methods. The reliability of results was checked by simulating two isothermal experimental profiles (i.e., at 250 and 300 °C) that were not used in the kinetic analysis. The predictions were in excellent agreement with the experimental data. This means that the torrefaction of olive pomace can be adequately described by a single-step model. The findings of the present study might open perspectives for the implementation of a computational model aimed at determining optimal torrefaction conditions with respect to the olive pomace.

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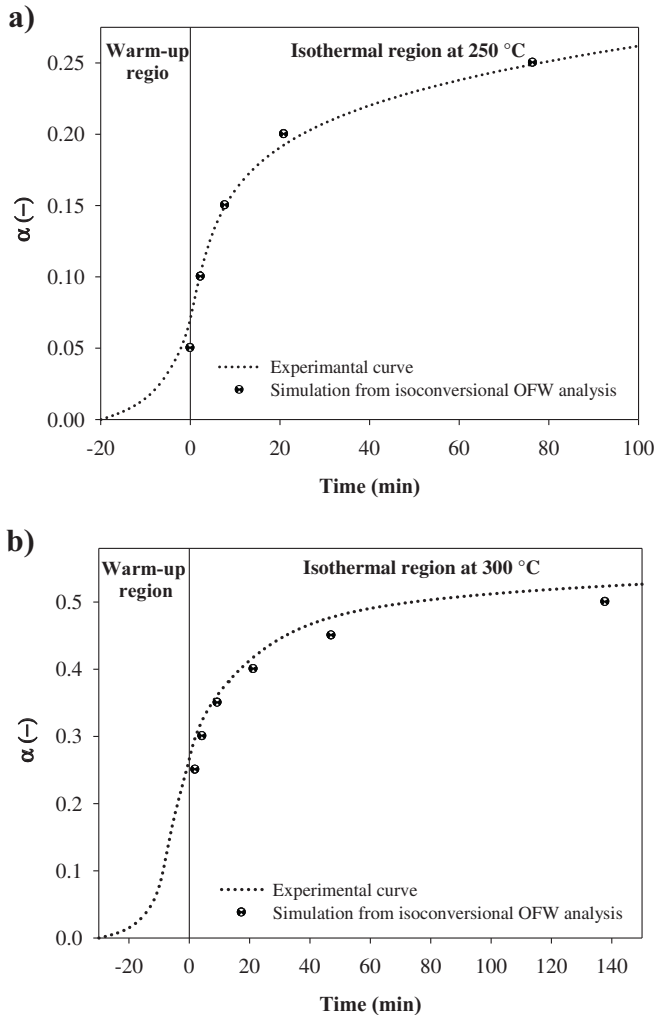


Fig. 6. Comparison of predicted data and experimental curve for olive pomace decomposition at: a) 250 °C and b) 300 °C.

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